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(54) Title: PROCESS FOR POLYMERIZING CATIONICALLY POLYMERIZABLE OLEFIN

(57) Abstract

A process for polymerizing a cationically polymerizable olefin such as a mixture of isoprene and isobutylene to produce butyl rubber. The process is conducted at subatmospheric pressure in the presence of a conventional cationic polymerization catalyst system. The preferred cationic polymerization catalyst system comprises Cp^*TiMe_3 and $\text{B}(\text{C}_6\text{H}_5)_3$. By conducting the process in this manner at subatmospheric pressure, a polymer having desirable molecular weight properties may be produced at a higher temperature than conventional means thereby lower capital and operating costs of the plant producing the polymer product.

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PROCESS FOR POLYMERIZING A CATIONICALLY POLYMERIZABLE OLEFIN

TECHNICAL FIELD

5 The present invention relates to a process for polymerizing at least one cationically polymerizable olefin.

BACKGROUND ART

Cationic polymerization of olefins is known in the art.

Conventional, cationic polymerization is effected using a catalyst system comprising: (i) a Lewis acid, (ii) a tertiary alkyl initiator molecule containing a halogen, ester, ether, acid or alcohol group, and, optionally, (iii) an electron donor molecule such as ethyl acetate. Such catalysts systems have been used for the so-called "living" and "non-living" carbocationic polymerization of olefins.

Component (ii) of the catalyst system typically is a compound having the formula:



25 wherein R¹, R² and R³ are a variety of alkyl or aromatic groups or combinations thereof, n is the number of initiator molecules and X is the functional group on which the Lewis acid effects a change to generate a carbocationic initiation site - i.e., X typically is a halogen, ester, ether, acid
30 or alcohol group depending on the Lewis acid employed. One or two X groups per initiator molecule tends to lead to the production of substantially linear

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polymers, whereas three or more X groups per initiator molecule tends to lead to the production of substantially star polymers.

Catalyst systems based on halogens and/or alkyl-containing Lewis acids, such as boron trichloride and titanium tetrachloride, use various combinations of the above components and typically have similar process characteristics. For the so-called "living" polymerization systems, it is conventional for Lewis acid concentrations to exceed the concentration of initiator sites by 16 to 40 times in order to achieve 100 percent conversion in 30 minutes (based upon a degree of polymerization equal to 890) at -75° to -80°C.

Examples of the so-called "living" polymerization systems are taught in United States patents 4,929,683 and United States patent 4,910,321, the contents of each of which are incorporated herein by reference. Specifically, these patents teach the use of Lewis acids in combination with organic acids, organic esters or organic ethers to form cationic polymerization initiators that also create a complex counter anion. Apparently, the complex counter anion does not assist in or cause proton elimination.

In the so-called "non-living" polymerization systems, high molecular weight polyisobutylenes are prepared practically only at low temperatures (-60 to -100°C) and at catalyst concentrations exceeding one catalyst molecule per initiator molecule. In practice, many of these catalyst systems are applicable only in certain narrow temperature regions and concentration profiles.

In recent years, a new class of catalyst systems utilizing compatible non-coordinating anions in combination with cyclopentadienyl transition metal compounds (also referred to in the art as "metallocenes") has been developed.

See, for example, any one of:

published European patent application 0,277,003A;

published European patent application 0,277,004;

United States patent 5,198,401; and

published International patent application WO92/00333.

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These references teach a method by which the metallocenes (biscyclopentadienyl and monocyclopentadienyl transition metal compounds) are protonated by an anionic precursor such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced
5 by the non-coordinating anion.

The use of ionizing compounds not containing an active proton is also known. See, for example, any one of:

published European patent application 0.426.637A; and
10 published European patent application 0.573.403A.

A further method of making ionic catalysts is disclosed in published European patent application 0,520,732A. Ionic catalysts for addition polymerization can also be prepared by oxidation of the metal centers of transition metal
15 compounds by anionic pre-cursors containing metallic oxidizing groups along with the anion groups - see, for example, published European patent application 0,495,375A.

It is also known in the art to immobilize the cationic polymerization catalyst system on an inert support material. Methods of supporting ionic
20 catalysts comprising metallocene cations and non-coordinating anions are described in:

published International patent application WO91/09882; and
published International patent application WO94/03506.

25

Further, United States patent 5,066,741 teaches the preparation of syndiotactic polystyrene or poly(vinyl aromatics) using non-coordinating anions in combination with cyclopentadienyl transition metal derivatives under coordination catalysis conditions. In United States patents 5,196,490 and
30 4,808,680 there is disclosed a similar procedure using an alumoxane.

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Jordan, in the Journal of the American Chemical Society (1986, 108, 1718-1719) teaches that tetraphenyl boron forms stable complexes with bis(cyclopentadienyl)zirconium dimethyl, unhindered Lewis bases such as 4,4'-dimethylbipyridine and 4-(dimethylamino) pyridine in CH₃CN. This reference
5 also teaches that tetraphenyl boron is stable in THF solution.

The polymerization of olefin monomers comprising isobutylene, including mixtures thereof with small amounts of isoprene to produce butyl rubber, present unique challenges. Specifically, as is well known in the art, since the polymerization reaction is highly exothermic, it is necessary to cool
10 the reaction mixture to approximately -95°C in large scale production facilities. This requirement has remained notwithstanding advances in the art relating to the development of novel reactor designs and/or novel catalyst systems.

Thus, it would be desirable to have a novel approach to polymerization of cationically polymerizable olefins, particularly olefins such as isobutylene
15 and mixtures thereof with diolefins (e.g., isoprene), which would allow for the polymerization reaction to be conducted under less stringent temperature regimes. It would be particularly useful if the novel approach could be readily adapted to existing production facilities.

20 DISCLOSURE OF THE INVENTION

It is an object of the present invention to obviate or mitigate at least one of the above-mentioned disadvantages of the prior art.

It is another object of the present invention to provide a novel process for polymerizing a cationically polymerizable olefin.

25 It is yet another object of the present invention to provide a novel process for polymerizing an olefin monomer comprising isobutylene.

Accordingly, in one of its aspects, the present invention provides a process for polymerizing a cationically polymerizable olefin comprising the step of polymerizing at least one cationically polymerizable olefin at a
30 subatmospheric pressure in the presence of a cationic polymerization catalyst system.

In another of its aspects the present invention provides a process for polymerizing an olefin monomer comprising isobutylene, the process comprising the step of polymerizing the olefin monomer at a subatmospheric pressure at a temperature higher than about -80°C in the presence of a cationic polymerization catalyst system.

Thus, the present inventor has surprisingly and unexpectedly discovered that it is possible to produce useful polymers by polymerizing a cationically polymerizable olefin at a subatmospheric pressure. This discovery is especially surprising and unexpected when applied to the polymerization of an olefin comprising isobutylene, optionally containing a diolefin such as isoprene. Specifically, the present process is applicable to the production of butyl rubber at temperatures higher than is conventional. This particular application of the process can result in significant savings in capital and operating expenses for a butyl rubber production facility.

BEST MODE FOR CARRYING OUT THE INVENTION

Thus, the present process is directed to the polymerization of at least one cationically polymerizable monomer. Of course the present process may be used to polymerize a mixture of monomers comprising the cationically polymerizable monomer. The mixture may comprise another cationically polymerizable monomer and/or another polymerizable monomer.

Preferably, the cationically polymerizable olefin is selected from the group comprising an olefin, a styrenic olefin, a heteroatom olefin and mixtures thereof.

Preferably, the olefin comprises a $\text{C}_2\text{-C}_{30}$ olefin, more preferably a $\text{C}_2\text{-C}_{20}$ olefin. Non-limiting examples of a useful olefin may be selected from the group comprising ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, dodecyldecene, 3-methylpentene-1, 3,5,5-trimethylhexene-1, isobutylene, 2-methyl-butene, 2-methyl-pentene, vinyl ether, vinyl carbazole and mixtures thereof.

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Preferably, the styrenic olefin is selected from the group comprising styrene, C₁-C₆₀ alkyl substituted styrene and mixtures thereof. Non-limiting examples of useful styrenic olefins may be selected from the group comprising styrene, α -methyl styrene, p-chlorostyrene, p-methylstyrene and mixtures thereof.

Preferably, the heteroatom olefin is selected from the group comprising alkyl vinyl ethers, alkyl, amines, alkenyl amines and aryl amines. Non-limiting examples of useful heteroatom olefins may be selected from the group comprising methyl vinyl ether, isobutylvinyl ether, butyl vinyl ether, vinyl carbazole and mixtures thereof.

A preferred monomer comprises a mixture of isobutylene and p-methyl styrene.

In a particularly preferred embodiment, polymerization is conducted in the presence of the at least one cationically polymerizable olefin and a diene monomer. The diene monomer may be conjugated or non-conjugated.

Diolefin monomers are well known in the art and the choice thereof for use in the present process is within the purview of a person skilled in the art. The non-conjugated diolefin can be straight chain, branched chain or cyclic hydrocarbon diolefins having from 6 to 15 carbon atoms. Illustrative nonlimiting examples are straight chain acyclic diolefins such as 1,4-hexadiene and 1,6-octadiene, the branched chain acyclic diolefins such as 5-methylhexadiene-1,4, 7-methyl-octadiene-1,6 and 7-methyl-octadiene-1,7; single ring alicyclic diolefins such as 1,4-cyclohexadiene and 1,5-cyclooctadiene, and multi ring alicyclic fused and bridged ring diolefins such as tetrahydroindene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene and 5-isopropylidene-2-norbornene. The conjugated diolefin is preferably selected from the group comprising 2,3-dimethyl-butadiene-1,3, isoprene, 1,3-butadiene and mixtures thereof.

As mentioned hereinabove, the present process is particularly advantageous in the preparation of butyl rubber polymers. The term "butyl rubber" as used throughout this specification is intended to denote polymers

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prepared by reacting a major portion, e.g., from about 70 to 99.5 parts by weight, usually 85 to 99.5 parts by weight of an isomonoolefin, such as isobutylene, with a minor portion, e.g., about 30 to 0.5 parts by weight, usually 15 to 0.5 parts by weight, of a multiolefin, e.g., a conjugated diolefin, such as isoprene or butadiene, for each 100 weight parts of these monomers reacted. The isoolefin, in general, is a C_4 to C_8 compound, e.g., isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene and 4-methyl-1-pentene. The preferred monomer mixture for use in the production of butyl rubber comprises isobutylene and isoprene. Optionally, an additional olefinic termonomer such as styrene, α -methylstyrene, p-methylstyrene, chlorostyrene, pentadiene and the like may be incorporated in the butyl rubber polymer. See, for example, any one of:

United States patent 2,631,984;
United States patent 5,162,445; and
United States patent 5,886,106.

The present process is conducted at subatmospheric pressure. Preferably, the pressure at which the present process is conducted is less than about 100 kPa, more preferably less than about 90 kPa, even more preferably in the range of from about 0.00001 to about 50 kPa, even more preferably in the range of from about 0.0001 to about 40 kPa, even more preferably in the range of from about 0.0001 to about 30 kPa, most preferably in the range of from about 0.0001 to about 15 kPa.

The present process comprises the use of a cationic polymerization system.

Preferably, the cationic polymerization system comprises a reactive cation and a compatible non-coordinating anion. The reactive cation may be any cation that can react with an olefin to create a carbocationic polymerization site.

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The terms "compatible non-coordinating anion" and "NCA" are used interchangeably throughout this specification and are intended to encompass an anion which either does not coordinate the cation or which is only weakly coordinated to the cation thereby remaining sufficiently labile to be displaced by an olefin monomer. Further, the term "compatible non-coordinating anion" specifically refers to an anion which, when functioning as a stabilizing anion in the cationic polymerization system used in the present process, does not irreversibly transfer an anionic substituent or fragment thereof to the cation thereby forming a neutral byproduct or other neutral compound. Compatible non-coordinating anions are anions which are not degraded to neutrality when the initially formed complex decomposes.

Non-limiting examples of such compatible non-coordinating anions may be selected from the group comprising alkyltris(pentafluorophenyl) boron ($\text{RB}(\text{pfp})_3^-$), tetra(pentafluorophenyl)boron ($\text{B}(\text{pfp})_4^-$), tetra(pentafluorophenyl)aluminum, carboranes, halogenated carboranes and the like.

For clarity, the formulae presented below depict the catalyst components in the "ionic" state. Of course, those of skill in the art will readily realize that many of these components are not stable as depicted and are obtained from a neutral stable form. For example, the species:



25

typically does not exist in this state alone. Rather, it is formed by reacting Cp_2ZrMe_2 with another compound that will abstract an Me group. This convention of describing the components in "ionic" form is used for descriptive purposes only and should not be construed as limiting in any way.

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The following references teach the neutral stable forms, and the synthesis of the cyclopentadienyl transition metal compositions and the NCA:

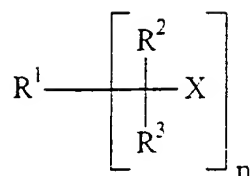
- published International patent application WO 92/00333;
5 published European patent application 0,129,368A;
published European patent application 0,551,277A
published European patent application 0,520,732A;
published European patent application 0,277,003A;
published European patent application 0,277,004A;
10 published European patent application 0,426,637A;
published European patent application 0,573,403A;
published European patent application 0,520,732A;
published European patent application 0,495,375A.
United States patent 5,017,714;
15 United States patent 5,055,438;
United States patent 5,153,157; and
United States patent 5,198,401.

For a description of compounds capable of producing the ionic species
20 in situ see either of published European patent applications 0,500,944A and
0,570,982A. These references teach in situ processes comprising the reaction
of alkyl aluminum compounds with dihalosubstituted metallocene compounds
prior to or with the addition of activating anionic compounds.

The neutral stable forms of the substituted carbocations and synthesis
25 thereof are described in United States patent 4,910,321, United States patent
4,929,683 and published European patent application 0,341,012A. In general,
the neutral stable form of such carbocations is typically represented by the
formula:

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5



wherein R_1 , R_2 , and R_3 are a variety of substituted or unsubstituted alkyl or aromatic groups or combinations thereof, n is the number of initiator molecules and is preferably greater than or equal to 1, even more preferably between 1 and 30, and X is the functional group on which the Lewis acid affects a change to bring about the carbocationic initiating site. This group is typically a halogen, ester, ether, alcohol or acid group depending on the Lewis acid employed.

For a discussion of stable forms of the substituted silylium and synthesis thereof, see F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, New York 1980. Likewise for stable forms of the cationic tin, germanium and lead compositions and synthesis thereof, see Dictionary of Organometallic compounds, Chapman and Hall New York 1984.

Thus, as stated hereinabove, the preferred cationic polymerization system comprises: (i) a reactive cation, and (ii) a non-coordinating anion.

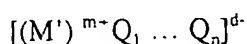
A preferred class of compatible non-coordinating anions includes chemically stable, non-nucleophilic substituted anionic complexes.

With reference to the non-coordinating anion, any metal or metalloid compound may be used that is capable of forming an anionic complex which is resistant to irreversibly transferring a substituent or fragment to the cation to neutralize the cation to produce a neutral molecule. In addition, any metal or metalloid capable of forming a coordination complex which is stable in water may also be used or contained in a composition comprising the anion. Suitable metals include, but are not limited to, boron, phosphorus, silicon and the like.

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Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

Preferably, the non-coordinating anion has the formula:



10

wherein:

M' is a metal or metalloid;

Q₁ to Q_n are, independently, bridged or unbridged hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any one, with the proviso that not more than one of Q₁ to Q_n may be a halide radical;

m is an integer representing the formal valence charge of M;

n is the total number of ligands Q; and

d is an integer greater than or equal to 1.

As set out above, it is to be understood that the anions herein are, in practice, counter balanced with a positively charged component that is removed before the anion acts with the reactive cation.

Non-limiting examples of a metal useful as M may be selected from the group comprising aluminum, gold and platinum. Non-limiting examples of a metalloid useful as M may be selected from the group comprising boron, phosphorus and silicon.

In a preferred embodiment:

M' is boron;

n=4;

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Q_1 and Q_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

5 Q_3 and Q_4 are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals, with the proviso that Q_3 and Q_4 will not be halide at the same time.

Non-limiting examples of boron components which may be used as
10 NCA's may be selected from the group comprising: tetra-valent boron compounds such as tetra(phenyl)boron, tetra(p-tolyl)boron, tetra(o-tolyl)boron, tetra(pentafluorophenyl)boron, tetra(o,p-dimethylphenyl)boron, tetra(m,m-dimethylphenyl)boron, (p-tri-fluoromethylphenyl)boron and mixtures thereof.

In a particularly preferred embodiment, $M = \text{boron}$, $n = 4$, Q_1 , Q_2 and
15 Q_3 are each (C_6F_5) and Q_4 is as defined above. Non-limiting examples of those preferred NCA's comprising boron triphenylmethyl salts where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymerix hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene or poly(paramethylstyrene).

20 Another preferred class of NCA's is the class comprising those NCA comprising a plurality of boron atoms, including boranes and carboranes. Non-limiting examples of carborane NCA's may be selected from the group comprising: dodecaborate, decachlorododecaborate, dodecachlorododecaborate, 1-carbadecaborate, 1-carbaundecaborate, 1-trimethylsilyl-1-carbadecaborate and
25 mixtures thereof. Non-limiting examples of borane and carborane complexes and salts of borane and carborane anions may be selected from the group comprising decaborane(14), 7,8-dicarbadecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, 6-carbadecaborate(12), 7-carbaundecaborate, 7,8-
30 dicarbaundecaborate.

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Further, NCA's comprising metallaborane anions are also useful. Non-limiting examples of such NCA's may be selected from the group comprising bis(nonahydrido-1,3-dicarbaboronaborato)cobaltate(III), bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III), bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III), bis(undecahydrido-7,8-dicarbaborato)nikelate(III), bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III), bis(undecahydridodicarbadodecaborato)cobaltate(III), bis(undecahydrido-7-carbaundecaborato)cobaltate(III) and mixtures thereof.

The NCA compositions most preferred for use in the cationic polymerization system are those containing a tris-perfluorophenyl boron, tetrapentafluorophenyl boron anion and/or two or more tripentafluorophenyl boron anion groups covalently bonded to a central atomic molecular or polymeric complex or particle.

The other component in the preferred cationic polymerization catalyst system comprises one or more reactive cations that are selected from different classes of cations and cation sources. Some preferred classes are:

(A) cyclopentadienyl transition metal complexes and derivatives thereof;

(B) substituted carbocations;

(C) substituted silylium;

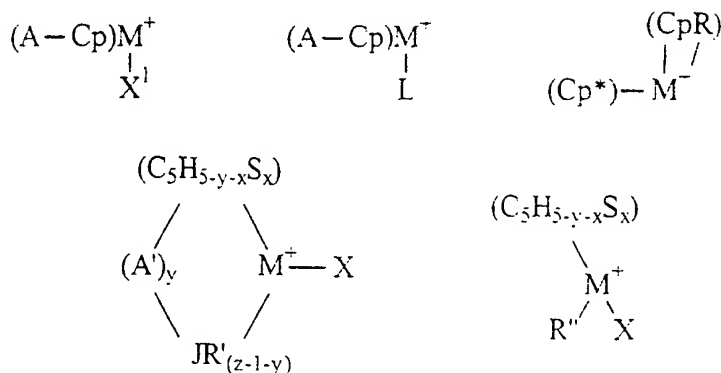
(D) compositions capable of generating a proton as further described below; and

(E) cationic compositions of germanium, tin or lead.

With reference to class (A), preferred cyclopentadienyl metal derivatives may be selected from the group comprising compounds that are a mono-, bis- or tris-cyclopentadienyl derivative of a transition metal selected from Groups 4, 5 or 6 of the Periodic Table of Elements. Preferred compositions include mono- cyclopentadienyl (Mono-Cp) or bis-cyclopentadienyl (Bis-Cp) Group 4 transition metal compositions, particularly zirconium, titanium and/or hafnium compositions.

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Preferred cyclopentadienyl derivatives are transition metal complexes selected from the group comprising:



wherein:

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp*;

- 5 Cp and Cp* are the same or different cyclopentadienyl rings substituted with from 0 to 5 substituent groups S, each substituent group S being, independently, a radical group selected from the group comprising hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid,
- 10 disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C₄ to C₂₀ ring system to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

- R is a substituent on one of the cyclopentadienyl radicals which is also
- 15 bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or (C₅H_{5-y-x}S_x) and JR'(_{z-1-y}) groups;

M is a Group 4,5, or 6 transition metal;

y is 0 or 1;

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(C₅H_{5-y-x}S_x) is a cyclopentadienyl ring substituted with from 0 to 5 S radicals;

x is from 0 to 5;

JR'(_{z-1-y}) is a heteroatom ligand in which J is a Group 15 element with a coordination number of three or a Group 16 element with a coordination number of 2, preferably nitrogen, phosphorus, oxygen or sulfur;

R" is a hydrocarbyl group;

X and X' are independently a hydride radical, hydrocarbyl radical, substituted hydrocarbyl radical, halocarbyl radical, substituted halocarbyl radical, and hydrocarbyl- and halocarbyl-substituted organometalloid radical, substituted pnictogen radical, or substituted chalcogen radicals; and

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base.

Other cyclopentadienyl compounds that may be used in the cationic polymerization catalyst system are described in:

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published European patent application 0,551,277A;

United States patent 5,055,438;

United States patent 5,278,119;

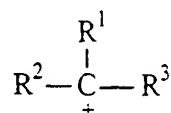
United States patent 5,198,401; and

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United States patent 5,096,867.

With reference to class (B), a preferred group of reactive cations comprises carbocationic compounds having the formula:

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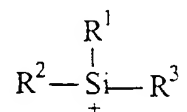
wherein R¹, R² and R³, are independently hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of R¹, R² and

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R³ may be hydrogen. Preferably, none of R¹, R² and R³ are H. Preferably, R¹, R² and R³, are independently a C₁ to C₂₀ aromatic or aliphatic group. Non-limiting examples of suitable aromatic groups may be selected from the group comprising phenyl, toluyl, xylyl and biphenyl. Non-limiting examples of
 5 suitable aliphatic groups may be selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.

With reference to class (C), a preferred group of reactive cations comprises substituted silylium cationic compounds having the formula:

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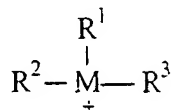
wherein R¹, R² and R³, are independently hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of R¹, R² and R³ may be hydrogen. Preferably, none of R¹, R² and R³ are H. Preferably, R¹, R² and R³ are, independently, a C₁ to C₂₀ aromatic or aliphatic group. More
 20 preferably, R¹, R² and R³ are independently a C₁ to C₈ alkyl group. Non-limiting examples of useful aromatic groups may be selected from the group comprising phenyl, toluyl, xylyl and biphenyl. Non-limiting examples of useful aliphatic groups may be selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and
 25 3,5,5-trimethylhexyl. A particularly preferred group of reactive substituted silylium cations may be selected from the group comprising trimethylsilylium, triethylsilylium and benzyldimethylsilylium. Such cations may be prepared by the exchange of the hydride group of the R¹R²R³Si-H with the NCA, such as Ph₃C⁺B(pfp)₄⁻ yielding compositions such as R¹R²R³SiB(pfp)₄ which in the
 30 appropriate solvent obtain the cation.

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With reference to class (D), the source for the cation may be any compound that will produce a proton when combined with the non-coordinating anion or a composition containing a non-coordinating anion. Protons may be generated from the reaction of a stable carbocation salt which contains a non-coordinating, non-nucleophilic anion with water, alcohol or phenol to produce the proton and the corresponding by-product. Such reaction may be preferred in the event that the reaction of the carbocation salt is faster with the protonated additive as compared with its reaction with the olefin. Other proton generating reactants include thiols, carboxylic acids, and the like. Similar chemistries may be realized with silylium type catalysts. In another embodiment, when low molecular weight polymer product is desired an aliphatic or aromatic alcohol may be added to inhibit the polymerization.

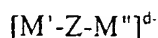
Another method to generate a proton comprises combining a Group 1 or Group 2 metal cation, preferably lithium, with water, preferably in a wet, non-protic organic solvent, in the presence of a Lewis base that does not interfere with polymerization. A wet solvent is defined to be a hydrocarbon solvent partially or fully saturated with water. It has been observed that when a Lewis base, such as isobutylene, is present with the Group 1 or 2 metal cation and the water, a proton is generated. In a preferred embodiment the non-coordinating anion is also present in the "wet" solvent such that active catalyst is generated when the Group 1 or 2 metal cation is added.

With reference to class (E), another preferred source for the cation is substituted germanium, tin or lead cations. Preferred non-limiting examples of such cations include substances having the formula:



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- wherein R^1 , R^2 and R^3 , are independently hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, and M is germanium, tin or lead with the proviso that only one of R^1 , R^2 and R^3 may be hydrogen. Preferably, none of R^1 , R^2 and R^3 are H. Preferably, R^1 , R^2 and R^3 are, independently, a C_1 to C_{20} aromatic or aliphatic group. Non-limiting examples of useful aromatic groups may be selected from the group comprising phenyl, tolyl, xyl, and biphenyl. Non-limiting examples of useful aliphatic groups may be selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.
- 10 A further preferred non-coordinating anion comprises a compound selected from the group comprising:



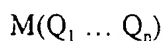
- 15 wherein:

d is an integer greater than or equal to 1;

Z is selected from the group comprising: OR' , SR' , SeR' , NR'_2 , PR'_2 , AsR'_2 , SbR'_2 , F, Cl, Br and I;

- R is selected from the group comprising hydrogen, C_1 - C_{40} alkyl, C_1 - C_{40} cycloalkyl, C_5 - C_{40} aryl, halogen substituted derivatives thereof and heteroatom substituted derivatives thereof;
- 20

M' and M'' may be the same or different and each has the formula



25

wherein:

M is a metal or metalloid;

- Q_1 to Q_n are, independently, bridged or unbridged hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any
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one, with the proviso that not more than one of Q_1 to Q_n may be a halide radical; and

n is an integer representing the formal valence charge of M .

Preferably, M is selected from the group comprising B, Al, Ga and In.

5 In this embodiment, the preferred non-coordinating anion is a tetra-valent boron compound. Non-limiting examples of such compounds may be selected from the group comprising tri(phenyl)boron, tri(p-tolyl)boron, tri(o-tolyl)boron, tri(pentafluorophenyl)boron, tri(o,p-dimethylphenyl)boron, tri(m,m-dimethylphenyl)boron and (p-tri-fluoromethylphenyl)boron.

10 Further details on the interaction of the reactive cation and the non-coordination anion of the preferred cationic polymerization system may be found in published International patent application WO 95/29940.

A particularly preferred type of cationic polymerization catalyst system is disclosed in United States patent 5,448,001. In some cases, it is possible to
15 use the coinitiator (BRR'R") disclosed in the '001 patent as the sole component of the cationic polymerization system in the present process. This approach is particularly well suited for the production of isobutylene-based polymers such as isobutylene homopolymer and the like.

As described above, the present process is particularly well suited for
20 the production of butyl rubber and other isobutylene-based polymers. Specifically, it has been discovered that such rubbers and polymers having desirable physical properties may be produced at higher temperatures than conventionally used.

Thus, the present process may be conducted at a temperature higher than
25 about -80°C , preferably at a temperature in the range of from about -80°C to about 25°C , more preferably at a temperature in the range of from about -40°C to about 25°C , even more preferably at a temperature in the range of from about -30°C to about 25°C , even more preferably at a temperature in the range of from about -20°C to about 25°C , most preferably at a temperature in the
30 range of from about 0°C to about 25°C .

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Embodiments of the present invention will be described with reference to the following Examples which are provided for illustrative purposes only and should not be used to limit the scope of or construe the invention.

5 EXAMPLES 1-4

All glassware was dried by heating at 120°C for at least 12 hours before being assembled in a nitrogen filled dry box. Nitrogen was purified by passing sequentially over heated BASF catalyst and molecular sieves. Dichloromethane was dried by refluxing over calcium hydride under nitrogen, toluene by
10 refluxing over sodium-benzophenone under nitrogen, and both solvents were freshly distilled under nitrogen immediately prior to use.

The diene monomers (isoprene (IP) or 2,3-dimethyl-1,3-butadiene, (DMBD)) were dried over molecular sieves and then distilled. Isobutylene (IB) was purified by passing through molecular sieve and barium oxide columns, and
15 condensed into a graduated flask immersed in liquid nitrogen. The IB was allowed to melt, the volume was noted (~3 to ~9 mL) and the IB was then refrozen by immersing in the liquid nitrogen bath. The system was evacuated to 10^{-1} to 10^{-2} torr, and the IB was melted and distilled at a temperature in the range of from about -10°C to about -6.5°C (the boiling point of IB being
20 -6.4°C at one atmosphere pressure) into the glass polymerization vessel; 6 mL of solvent (toluene) was added to the condenser which was attached to the reactor; and the solution of IB was brought to the desired temperature (usually approximately
-30°C).

25 Solutions of Cp^*TiMe_3 ($\text{Cp}^* \equiv \eta^5\text{-pentamethylcyclopentadienyl}$; Me \equiv methyl; usually 14 mg, 0.06 mmol; recrystallized from pentane) and $\text{B}(\text{C}_6\text{F}_5)_3$ (usually 32 mg, 0.06 mmol; sublimed), both in 1-2 mL of solvent, were added sequentially to provide an initiator to monomer ratio of approximately 1:1500.

In some Examples, an amount of diene equivalent to ~1% (mole) of the
30 amount of IB was added to the reaction vessel prior to the addition of initiator and co-initiator.

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Solutions of olefin(s) and initiator system were generally stirred as long as possible under a static vacuum and at the predetermined temperature (by "static vacuum", it is meant that the system was closed at this point and the pressure essentially was the vapour pressure of PIB at the reaction temperature).

- 5 Copious amounts of polymeric materials generally began to precipitate after about 2 minutes, and reactions were terminated after 10-30 min by the addition of 5-10 mL methanol. The precipitated polymeric materials were purified of inorganic residues by dissolving in pentane or hexane and passing through a short silica column. Solvents were removed under reduced pressure and the
10 solid, white polymers were dried at 60°C-90°C for at least two days. Control reactions were also run using just Cp^*TiMe_3 or $\text{B}(\text{C}_6\text{F}_5)_3$.

In Table 1, there is reported the use of vacuum (where vacuum was not used, polymerization was conducted under $\text{Ar}(\text{g})$ at atmospheric pressure), the presence/absence of isoprene comonomer, the polymerization temperature (T),
15 the weight average molecular weight of the polymer product (M_w) and the polydispersity index (M_w/M_n) of the polymer product.

Table 1

Example	Vacuum	Comonomer	T	$M_w, \times 10^4$	M_w/M_n
20 1	No	No	-32°C	41.3	2.0
2	Yes	No	-32°C	61.6	2.0
3	No	Yes	-30°C	11.6	1.6
4	Yes	Yes	-30°C	14.4	1.8

25

As will be apparent to those of skill in the art, a vacuum was not applied during polymerization in Examples 1 and 3. Accordingly, Examples 1 and 3 are provided for comparative purposes only and are not encompassed by the present invention.

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The results in Table 1 support the conclusion that conducting the polymerization of isobutylene at subatmospheric pressure (Example 2) results in the production of a polymer having a higher Mw when compared to conducting the polymerization of isobutylene at atmospheric pressure (Example 1). Similarly, the results in Table 1 support the conclusion that conducting the polymerization of isobutylene/isoprene at subatmospheric pressure (Example 4) results in the production of a copolymer having a higher Mw when compared to conducting the polymerization of isobutylene/isoprene at atmospheric pressure (Example 3).

10

All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

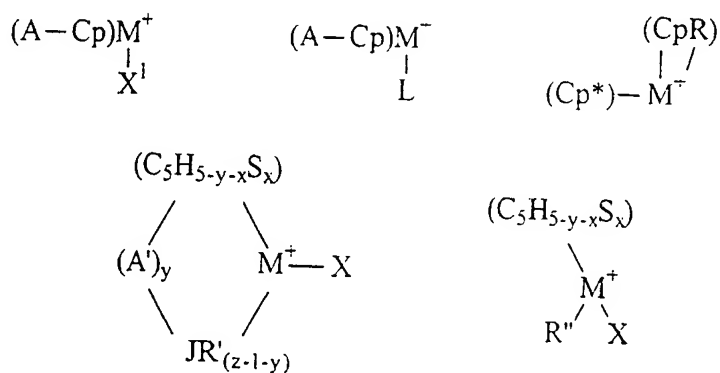
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What is claimed is:

1. A process for polymerizing a cationically polymerizable olefin comprising the step of polymerizing at least one cationically polymerizable olefin at a subatmospheric pressure in the presence of a cationic polymerization catalyst system.
2. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature higher than about -80°C .
3. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature in the range of from about -80°C to about 25°C .
4. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature in the range of from about -40°C to about 25°C .
5. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature in the range of from about -30°C to about 25°C .
6. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature in the range of from about -20°C to about 25°C .
7. The process defined in claim 1, wherein said step of polymerizing is conducted at a temperature in the range of from about 0°C to about 25°C .
8. The process defined in any one of claims 1-7, wherein the subatmospheric pressure is less than about 100 kPa.
9. The process defined in any one of claims 1-7, wherein the subatmospheric pressure is less than about 90 kPa.

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10. The process defined in any one of 1-7, wherein the subatmospheric pressure is in the range of from about 0.00001 to about 50 kPa.
11. The process defined in any one of claims 1-7, wherein the subatmospheric pressure is in the range of from about 0.0001 to about 40 kPa.
12. The process defined in any one of claims 1-7, wherein the subatmospheric pressure is in the range of from about 0.0001 to about 30 kPa.
13. The process defined in any one of claims 1-7, wherein the subatmospheric pressure is in the range of from about 0.0001 to about 15 kPa.
14. The process defined in any one of claims 1-13, wherein the cationic polymerization system comprises: (i) a reactive cation, and (ii) a non-coordinating anion.
15. The process defined in claim 14, wherein the reactive cation comprises a cyclopentadienyl transition metal complex.
16. The process defined in claim 15, wherein the transition metal complex comprises a compound selected from the group comprising:



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wherein:

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp*;

Cp and Cp* are the same or different cyclopentadienyl rings substituted with from 0 to 5 substituent groups S, each substituent group S being, independently, a radical group selected from the group comprising hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen or halogen radicals, or Cp and Cp* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C₄ to C₂₀ ring system to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp* rings or (C₅H_{5-y-x}S_x) and JR'(_{z-1-y}) groups:

M is a Group 4,5, or 6 transition metal;

y is 0 or 1;

(C₅H_{5-y-x}S_x) is a cyclopentadienyl ring substituted with from 0 to 5 S radicals;

x is from 0 to 5;

JR'(_{z-1-y}) is a heteroatom ligand in which J is a Group 15 element with a coordination number of three or a Group 16 element with a coordination number of 2, preferably nitrogen, phosphorus, oxygen or sulfur;

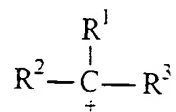
R" is a hydrocarbyl group;

X and X¹ are independently a hydride radical, hydrocarbyl radical, substituted hydrocarbyl radical, halocarbyl radical, substituted halocarbyl radical, and hydrocarbyl- and halocarbyl-substituted organometalloid radical, substituted pnictogen radical, or substituted chalcogen radicals; and

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base.

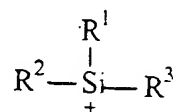
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17. The process defined in claim 14, wherein the reactive cation comprises a cationic compound having the formula:



wherein R^1 , R^2 and R^3 are, independently, hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of R^1 , R^2 and R^3 may be hydrogen.

18. The process defined in claim 17, wherein none of R^1 , R^2 and R^3 are H.
19. The process defined in claim 17, wherein R^1 , R^2 and R^3 are, independently, a C_5 to C_{20} aromatic or a C_1 to C_{20} aliphatic group.
20. The process defined in claim 19, wherein the aromatic group is selected from the group comprising phenyl, tolyl, xylyl and biphenyl.
21. The process defined in claim 19, wherein the aliphatic group is selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.
22. The process defined in claim 14, wherein the reactive cation comprises a cationic compound having the formula:



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wherein R^1 , R^2 and R^3 are, independently, hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of R^1 , R^2 and R^3 may be hydrogen.

23. The process defined in claim 22, wherein none of R^1 , R^2 and R^3 are H.

24. The process defined in claim 22, wherein R^1 , R^2 and R^3 are, independently, a C_5 to C_{20} aromatic or a C_1 to C_{20} aliphatic group.

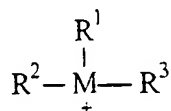
25. The process defined in claim 22, wherein R^1 , R^2 and R^3 are, independently, a C_1 to C_8 alkyl group.

26. The process defined in claim 24, wherein the aromatic group is selected from the group comprising phenyl, tolyl, xylyl and biphenyl.

27. The process defined in claim 24, wherein the aliphatic group is selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.

28. The process defined in claim 14, wherein the reactive cation comprises a cationic compound selected from the group comprising trimethylsilylium, triethylsilylium and benzyldimethylsilylium.

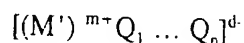
29. The process defined in claim 14, wherein the reactive cation comprises a cationic compound having the formula:



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wherein R^1 , R^2 and R^3 are, independently, hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, and M is germanium, tin or lead with the proviso that only one of R^1 , R^2 and R^3 may be hydrogen.

30. The process defined in claim 29, wherein none of R^1 , R^2 and R^3 are H.
31. The process defined in claim 29, wherein R^1 , R^2 and R^3 are, independently, a C_5 to C_{20} aromatic or a C_1 to C_{20} aliphatic group.
32. The process defined in claim 31, wherein the aromatic group is selected from the group comprising phenyl, tolyl, xylyl and biphenyl.
33. The process defined in claim 31, wherein the aliphatic group is selected from the group comprising methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.
34. The process defined in any one of claims 14-33, wherein the non-coordinating anion has the formula:



wherein:

M' is a metal or metalloid;

Q_1 to Q_n are, independently, bridged or unbridged hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any one, with the proviso that not more than one of Q_1 to Q_n may be a halide radical;

m is an integer representing the formal valence charge of M ;

n is the total number of ligands Q ; and

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d is an integer greater than or equal to 1.

35. The process defined in claim 34, wherein the metal is selected from the group comprising aluminum, gold and platinum.

36. The process defined in claim 34, wherein the metalloid is selected from the the group comprising boron, phosphorus and silicon.

37. The process defined in claim 34, wherein

M' is boron;

n=4;

Q₁ and Q₂ are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

Q₃ and Q₄ are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted pnictogen radicals, substituted chalcogen radicals and halide radicals, with the proviso that Q₃ and Q₄ are not halide at the same time.

38. The process defined in claim 37, wherein:

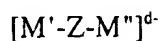
M' is boron;

n = 4;

Q₁, Q₂ and Q₃ are each (C₆F₅); and

Q₄ is as defined above.

39. The process defined in any one of claims 14-33, wherein the non-coordinating anion comprises a compound selected from the group comprising:



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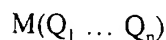
wherein:

d is an integer greater than or equal to 1;

Z is selected from the group comprising: OR^- , SR^- , SeR^- , NR_2^- , PR_2^- , AsR_2^- , SbR_2^- , F^- , Cl^- , Br^- and I^- ;

R is selected from the group comprising hydrogen, C_1 - C_{40} alkyl, C_1 - C_{40} cycloalkyl, C_5 - C_{40} aryl, halogen substituted derivatives thereof and heteratom substituted derivatives thereof;

M' and M'' may be the same or different and each has the formula



wherein:

M is a metal or metalloid;

Q_1 to Q_n are, independently, bridged or unbridged hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl and halocarbyl-substituted organometalloid radicals and any one, with the proviso that not more than one of Q_1 to Q_n may be a halide radical; and

n is an integer representing the formal valence charge of M.

40. The process defined in claim 39, wherein M is selected from the group comprising B, Al, Ga and In.

41. The process defined in any one of claims 14-33, wherein the non-coordinating anion is a tetra-valent boron compound.

42. The process defined in claim 41, wherein the tetra-valent boron compound is selected from the group comprising tri(phenyl)boron, tri(p-tolyl)boron, tri(o-tolyl)boron, tri(pentafluorophenyl)boron, tri(o,p-

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dimethylphenyl)boron, tri(m,m-dimethylphenyl)boron and (p-tri-fluoromethylphenyl)boron.

43. The process defined in any one of claims 14-33, wherein the non-coordinating anion is selected from the group comprising boranes and carboranes.

44. The process defined in any one of claims 14-33, wherein the non-coordinating anion is selected from the group comprising dodecaborate, decachlorododecaborate, dodecachlorododecaborate, 1-carbadecaborate, 1-carbaundecaborate, 1-trimethylsilyl-1-carbadecaborate.

45. The process defined in any one of claims 14-33, wherein the non-coordinating anion is selected from the group comprising decaborane(14), 7,8-dicarbadecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, 6-carbadecaborate(12), 7-carbaundecaborate and 7,8-dicarbaundecaborate.

46. The process defined in any one of claims 14-33, wherein the non-coordinating anion comprises a metalloborane anion selected from the group comprising bis(nonahydrido-1,3-dicarbaborato)cobaltate(III), bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III), bis(undecahydrido-7,8-dicarbaundecaborato) cobaltate(III), bis(undecahydrido-7,8-dicarbaborato) nikelate(III), bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III), bis(undecahydridodicarbadoecaborato)cobaltate(III) and bis(undecahydrido-7-carbaundecaborato) cobaltate(III).

47. The process defined in any one of claims 1-46, wherein said step of polymerizing is conducted under substantially anhydrous conditions.

48. The process defined in any one of claims 1-47, wherein said step of polymerizing is conducted in the substantial absence of a diluent.
49. The process defined in any one of claims 1-47, wherein said step of polymerizing is conducted in the presence of a diluent.
50. The process defined in claim 49, wherein the diluent is selected from the group comprising polar diluents, non-polar diluents and mixtures thereof.
51. The process defined in claim 49, wherein the diluent is selected from the group comprising haloaromatic compounds, hexane, heptane, halogenated hydrocarbons and mixtures thereof.
52. The process defined in claim 49, wherein the diluent is selected from the group comprising methyl cyclohexane, ethyl cyclohexane, propyl cyclohexane, chlorobenzene, bromobenzene, fluorobenzene, iodobenzene, methyl chloride, methylene chloride, ethyl chloride, propyl chloride, butyl chloride, chloroform and mixtures thereof.
53. The process defined in any one of claims 1-52, wherein at least one cationically polymerizable olefin is selected from the group comprising an olefin, a styrenic olefin, a heteroatom olefin and mixtures thereof.
54. The process defined in claim 53, wherein the olefin comprises a C₂-C₃₀ olefin.
55. The process defined in claim 53, wherein the olefin comprises a C₂-C₂₀ olefin.

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56. The process defined in claim 53, wherein the olefin is selected from the group comprising ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, dodecyldocecene, 3-methylpentene-1, 3,5,5-trimethylhexene-1, isobutylene, 2-methyl-butene, 2-methyl-pentene, vinyl ether, vinyl carbazole and mixtures thereof.

57. The process defined in claim 53, wherein the styrenic olefin is selected from the group comprising styrene, C_1 - C_{60} alkyl substituted styrene and mixtures thereof.

58. The process defined in claim 53, wherein the styrenic olefin is selected from the group comprising styrene, α -methyl styrene, p-chlorostyrene and p-methylstyrene and mixtures thereof.

59. The process defined in claim 53, wherein the heteroatom olefin is selected from the group comprising alkyl vinyl ethers, alkyl amines, alkenyl amines and aryl amines.

60. The process defined in claim 53, wherein the heteroatom olefin is selected from the group comprising methyl vinyl ether, isobutylvinyl ether, butyl vinyl ether, vinyl carbazole and mixtures thereof.

61. The process defined in any one of claims 1-52, wherein the at least one cationically polymerizable olefin comprises a mixture of isobutylene and p-methyl styrene.

62. The process defined in any one of claims 1-60, wherein said step of polymerization is conducted in the presence of the at least one cationically polymerizable olefin and a diene monomer.

-34-

63. The process defined in claim 62, wherein the diene monomer is conjugated.

64. The process defined in any one of claims 1-60, wherein the at least one cationically polymerizable olefin comprises a mixture of isobutylene and isoprene.

65. The process defined in claim 62, wherein the diene monomer is unconjugated.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 99/00644

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F10/10 C08F4/643

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 21700 A (EXXON CHEMICAL PATENTS INC) 29 September 1994 (1994-09-29)	1-16, 34, 36-41, 49-51, 53-56
Y	examples 1,10	1,14, 17-38, 41-46
	claims 1,5-8	
Y	WO 95 29940 A (EXXON CHEMICAL PATENTS INC) 9 November 1995 (1995-11-09) cited in the application abstract page 5, line 33 -page 12, line 25 examples A,C,D,E	1,14, 17-38, 41-46
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 99/00644

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	<p>US 5 635 573 A (HARRINGTON BRUCE A ET AL) 3 June 1997 (1997-06-03)</p> <p>column 29 -column 30; example 42; table 2 claims 1,2</p>	<p>1.2, 8-11, 14-16, 34,36, 41, 49-51, 53-56</p>
X	<p>EP 0 277 003 A (EXXON CHEMICAL PATENTS INC) 3 August 1988 (1988-08-03) cited in the application</p> <p>example 24 claim 11</p>	<p>1.2.8.9. 14-16, 34,44, 45, 49-51, 53-56</p>
X	<p>BOCHMANN M ET AL: "Cationic group IV metal alkyl complexes and their role as olefin polymerization catalysts: The formation of ethyl-bridged dinuclear and heterodinuclear zirconium and hafnium complexes" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 497, no. 1, 26 July 1995 (1995-07-26), page 55-59 XP004023842 ISSN: 0022-328X page 57; table 1</p>	<p>1-7, 14-16, 34,36, 41, 49-51, 53-56</p>
A	<p>EP 0 277 004 A (EXXON CHEMICAL PATENTS INC) 3 August 1988 (1988-08-03) cited in the application examples 1,2</p>	<p>1</p>
A	<p>US 5 066 741 A (CAMPBELL JR RICHARD E) 19 November 1991 (1991-11-19) cited in the application column 8, line 29 - line 34 claims 1-3</p>	<p>1</p>

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